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Electrical charging changes the composition of sulfuric acid-ammonia/dimethylamine clusters

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Abstract

Sulfuric acid clusters stabilized by base molecules are likely to have a significant role in atmospheric new particle formation. Recent advances in mass spectrometry techniques have permitted the detection of electrically charged clusters. However, direct measurement of electrically neutral clusters is not possible. Mass spectrometry instruments can be combined with a charger, but the possible effect of charging on the composition of neutral clusters must be addressed before the measured data can be linked to properties of neutral clusters. In the present work we have used formation free energies from quantum chemical methods to calculate the evaporation rates of electrically charged (both positive and negative) sulfuric acid-ammonia/dimethylamine clusters. To understand how charging will affect the composition of these clusters, we have compared the evaporation rates of charged clusters with those of the corresponding neutral clusters. We found that the only cluster studied in this paper which will retain its composition is $H_2SO_4 \cdot NH_3$ when charged positively; all other clusters will be altered by both positive and negative charging. In the case of charging clusters negatively, base molecules will completely evaporate from clusters with 1 to 3 sulfuric acid molecules in the case of ammonia, and from clusters with 1 or 2 sulfuric acid molecules in the case of dimethylamine. Larger clusters will maintain some base molecules, but the H_2SO_4 : base ratio will increase. In the case of positive charging, some of the acid molecules will evaporate, decreasing the H_2SO_4 : base ratio.

1 Introduction

Atmospheric aerosol particles affect climate both directly and indirectly (IPCC, 2007; Merikanto et al., 2009). One of the less understood aerosol related processes is the formation of new particles from condensable vapors in the atmosphere. The participation of sulfuric acid in this process is clear (see, for example, Sipilä et al., 2010), but sulfuric acid on its own cannot explain the new particle formation rates observed during different field campaigns. It has been known for long that sulfuric acid clusters need to be stabilized to be able to form aerosol particles. The identity of these stabilizing compounds has been the subject of several studies during the recent years. Ammonia has been one of the most studied candidates to stabilize sulfuric acid clusters (Weber et al., 1996; Merikanto et al., 2007; Benson et al., 2010). Recent results from the state-of-the-art CLOUD experiment at CERN (Kirkby et al., 2011) have shown that, although the presence of ammonia can enhance the observed particle formation rate, the rates measured in the experiment are still far from those observed in the atmosphere. Organic compounds, especially organic nitrogen bases such as amines, have become the strongest candidate to explain observed formation rates. In 2001 Mäkelä et al. reported the presence of amines in particles during new particle formation events (Mäkelä et al., 2001). Different quantum chemical studies have shown that amines stabilize sulfuric acid clusters more efficiently than ammonia (Kurtén et al., 2008; Loukonen et al., 2010; Nadykto et al., 2011). This is supported by atmospheric and laboratory measurements (Smith et al., 2010; Zhao et al., 2011; Almeida et al., 2013).

The main problem in understanding new-particle formation is that the key steps occur in small molecular clusters, below 1.5 nm in diameter (see for example, Kulmala et al., 2013). Recent developments in cutting-edge high-resolution mass spectrometry have enabled the chemical characterization of charged clusters from the molecular scale upward (Junninen et al., 2010; Ehn et al., 2011; Kirkby et al., 2011; Kulmala et al., 2013). These measurements can only provide the elemental composition of the detected clusters, which makes it impossible to distinguish between different compounds with the same elemental formula. For example, the compound with the elemental formula C_3H_7N can be either dimethylamine ($(CH_3)_2NH$) or ethylamine ($CH_3CH_2NH_2$). In addition, these measurements alone yield no information on the composition of neutral clusters. A charger can be included in front of the mass spectrometer (Jokinen et al., 2012), but depending on the charging mechanism used in the instruments, some cluster types may not be charged, others may be broken up and others may be chemically completely altered by the process (Kurtén et al., 2011; Kupiainen-Määttä et al., 2013;

Ruusuvuori et al., 2013). Furthermore, clusters sampled by the Atmospheric Pressure Interface-Time of Flight Mass Spectrometer (APi-TOF-MS) pass through a low pressure interface, where loosely bound molecules can evaporate from the clusters. In addition, high energy collisions with gas molecules inside the instrument can also affect the composition of the detected clusters.

In the present work, we have used the formation free energies from our previous quantum chemistry based works (Kupiainen et al., 2012; Olenius et al., 2013a, b) to calculate the evaporation rate of charged sulfuric acid – ammonia and sulfuric acid – dimethylamine (DMA) clusters. We present a detailed analysis of the stability of charged clusters with different compositions. In addition we compare the evaporation rates of the charged clusters to those of the corresponding neutral clusters, calculated in our previous work (Ortega et al., 2012), to determine how the charging process will affect the neutral clusters.

2 Methodology

In this work we have used the formation free energies calculated in our previous works (Kupiainen et al., 2012; Olenius et al., 2013a, b) using a multi-step quantum chemical method developed by our group (Ortega et al., 2012). The geometry optimizations and frequency calculations were performed with the Gaussian09 program (Frisch et al., 2009) using the B3LYP hybrid functional (Becke, 1993) and a CBSB7 basis set (Montgomery et al., 1999), and a single-point electronic energy was then calculated with the TURBOMOLE program (Ahlrichs et al., 1989) using the RI-CC2 method (Hättig and Weigend, 2000) and an aug-cc-pV(T + d)Z basis set (Dunning et al., 2001). We will refer to this method as B3RICC2.

In a previous study (Ortega et al., 2012) we compared the results obtained with the B3RICC2 method with those of the high level multi-step method CBS-QB3 (Montgomery et al., 1999). The agreement between these two methods was very good (with an average difference of 0.74 kcal mol^{-1}). Unfortunately, experimental measurements of Gibbs formation free energies of the neutral clusters studied here do not exist. Present experimental techniques to estimate the Gibbs formation free energies are based on mass spectrometry measurements, and thus only charged clusters can be studied. This leaves theoretical methods, out of which quantum chemistry is currently the most accurate method, as the only way to determine Gibbs formation free energies of neutral clusters. Experimental Gibbs formation free energies exist for some of the charged clusters studied in this work (Lovejoy et al., 2003). For these cases a direct comparison between quantum chemical and experimental results is possible.

The evaporation rate of a certain molecule or cluster, $\gamma_i(N_i)$, from the cluster N_{i+j} is related to the Gibbs formation free energies through the equation (see, for example, Ortega et al., 2012 and references therein)

$$\gamma_i(N_{i+j}) = \beta_{\mathrm{ij}} c_{\mathrm{ref}} \exp\left(\frac{\Delta G(N_{i+j}) - \Delta G(N_i) - \Delta G(N_j)}{kT}\right) \tag{1}$$

where β_{ij} is the collision rate of N_i with N_j, $\Delta G(N_{i+j})$, $\Delta G(N_i)$ and $\Delta G(N_j)$, are the Gibbs free energies of formation of clusters N_{i+j}, N_i and N_j from monomers at the reference vapour concentration c_{ref}, k is the Boltzmann constant and T is the temperature. It must be noted that in the case where N_i and/or N_j are monomers, $\Delta G(N_i)$ and/or $\Delta G(N_j)$ are by definition zero.

The collisions rate of a charged cluster with a neutral cluster can be calculated as (Su and Browers, 1973)

$$\beta_{\mathrm{ij}} = \frac{\mathrm{Ze}}{2\varepsilon_0}\left(\frac{1}{m_i} + \frac{1}{m_j}\right)^{\frac{1}{2}} \times \left[(4\pi\varepsilon_0\alpha_j)^{\frac{1}{2}} + c\mu_j\left(\frac{2}{\pi kT}\right)^{\frac{1}{2}}\right] \tag{2}$$

where Ze is the charge of the ionic cluster, ε_0 is the vacuum permittivity, m_i and m_j are the masses of the colliding clusters, α_j and μ_j are the polarizability and the dipole moment of the colliding neutral molecule/cluster, respectively, and c is a scaling factor related to the orientation of the dipole moment towards the colliding ion. As suggested by Su and Bowers (1973) a value of 0.15 for the scaling factor c has been used. The polarizabilities and dipole moments used are summarized in Supplement Table S1.

3 Benchmarking computational results against experiments

Table 1 shows the comparison of the evaporation rates deduced from experimental formation free energies (Lovejoy et al., 2003) with those obtained using formation free energies from quantum chemistry.

In the case of the $H_2SO_4 \cdot HSO_4^-$ cluster, the B3RICC2 method underestimates the experimental evaporation rate by 3–4 orders of magnitude, while for all other clusters it is able to reproduce the experimental values accurately with deviations below one order of magnitude, corresponding to an average difference of 0.44 $\mathrm{kcal\,mol^{-1}}$ in the formation free energies. The disagreement in the evaporation rate of $H_2SO_4 \cdot HSO_4^-$ may be due to the presence of an almost free internal rotation in the HSO_4^- ion, which is incorrectly modeled as a low-frequency vibration (Kurtén et al., 2007; Ortega et al., 2008). This would explain why the error is only found in the charged dimer, as it will cancel out when computing the addition energies of sulfuric acid to form larger clusters. Although the difference between the calculated value and the experimental one for $H_2SO_4 \cdot HSO_4^-$ cluster is large, the evaporation rate of the charged dimer is so small that it does not in practice evaporate at all in any case. If we consider that the collision rate of sulfuric acid molecules with one charged dimer is about $10^{-9}\,\mathrm{s^{-1}\,cm^{-3}}$ and the atmospheric concentration of sulfuric acid is between 10^6 and $10^7\,\mathrm{cm^{-3}}$, an evaporation rate smaller than 10^{-2}–$10^{-3}\,\mathrm{s^{-1}}$ will be enough to allow further acid collisions before the dimer evaporates. Therefore, the differences between the quantum chemical and experimental evaporation rates for the charged dimer will not have an effect in terms of cluster kinetics at atmospherically relevant sulfuric acid concentration.

4 Results

We have used the formation free energies calculated for sulfuric acid–ammonia and sulfuric acid–DMA charged clusters from previous works (Kupiainen et al., 2012; Olenius et al., 2013a, b) to calculate their evaporation rates. We have included negatively and positively charged clusters containing up to four sulfuric acid and four DMA molecules and up to five sulfuric acid and five ammonia molecules. In the case of negatively charged DMA-containing clusters, $(H_2SO_4)_3 \cdot HSO_4^- \cdot ((CH_3)_2NH)_2$ cluster is already more stable than $(H_2SO_4)_3 \cdot HSO_4^-$ cluster. On the other hand, for negatively charged ammonia-containing clusters, $(H_2SO_4)_3 \cdot HSO_4^- \cdot (NH_3)_2$ cluster is as stable as $(H_2SO_4)_3 \cdot HSO_4^-$ cluster. To check if larger ammonia-containing clusters were more stable than the corresponding pure (with no base molecules) negatively charged sulfuric acid cluster, as in the case of DMA-containing clusters, we extended the analysis up to the negatively charged pentamers in the case of ammonia. Some clusters with an unfavorable acid-base ratio have been left out due to their relatively low stability, as discussed by Olenius et al. (2013a). Tables 2a and 2b summarize the specific negative and positive clusters included in this study.

Figure 1 shows the structures of most stable clusters with one to four (or five in the case of pure sulfuric acid and ammonia-containing clusters) sulfuric acid molecules for: (A) negatively charged sulfuric acid clusters, (B) negatively charged ammonia-containing clusters, (C) negatively charged DMA-containing clusters, (D) positively charged ammonia-containing clusters and (E) positively charged DMA-containing clusters (xyz coordinates for all clusters included in the study are provided in the supplementary material). Note that in the case of negatively charged base-containing clusters the most stable cluster refers to the most stable cluster with at least one base molecule, not to the most stable negatively charged cluster overall. Negatively charged DMA-containing clusters needs at least three sulfuric acid molecules (including the bisulfate ion) to have a low enough evaporation rate to be abundant under atmospheric, while in the case of ammonia-containing clusters four sulfuric acid molecules (including the bisulfate ion) are needed. For negative clusters containing four acids, the most stable clusters contain two base molecules, both in the case of DMA and ammonia. The second DMA molecule accepts a proton from the HSO_4^- ion, forming a sulfate ion (SO_4^{2-}). The sulfate ion is also formed in $(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_3$ cluster.

The general structures of the most stable positively charged clusters are similar for both the ammonia and DMA containing systems. All base molecules are found in their protonated form as long as the cluster contains enough sulfuric acid molecules to donate the protons. Unsurprisingly, the sulfate ion (SO_4^{2-}) is never formed in positively charged clusters. The composition of the most stable positively charged clusters can be summarized as $(HSO_4^-)_x \cdot (NH_4^+)_{x+1} // ((CH_3)_2NH_2^+)_{x+1}$.

4.1 Negative clusters

In our previous work (Ortega et al., 2012) we showed that, based on the computed Gibbs formation energies, cluster-fission processes were more important than monomer evaporation for some neutral clusters. Thus, in the present work, we have calculated the monomer evaporation rates and all the possible cluster fission rates. Table 3 summarizes the highest evaporation rates for each cluster as well as the evaporated molecule/cluster. As in the neutral system, cluster-fission is only relevant for DMA-containing clusters. The fragments leaving the cluster in the fission process are $(H_2SO_4)_2 \cdot (CH_3)_2NH$ and $(H_2SO_4)_2 \cdot ((CH_3)_2NH)_2$ which are extremely stable (Ortega et al., 2012).

Evaporation rates of pure sulfuric acid, sulfuric acid–ammonia and sulfuric acid–DMA clusters at 298.15 K are compared in Fig. 2. The negatively charged sulfuric acid dimer, $H_2SO_4 \cdot HSO_4^-$, is extremely stable with an evaporation rate of practically zero. The negatively charged sulfuric acid trimer, $(H_2SO_4)_2 \cdot HSO_4^-$, is also stable, with an evaporation rate of $3.67 \times 10^{-3}\,s^{-1}$. The collision frequency of free sulfuric acid molecules with one charged trimer is $1.23 \times 10^{-9}\,s^{-1}\,cm^{-3}$. Thus, if the concentration of sulfuric acid monomers is $3 \times 10^{6}\,cm^{-3}$ or larger, the collisions of sulfuric acid monomers with the cluster will be faster than evaporation. In case of the charged tetramer, $(H_2SO_4)_3 \cdot HSO_4^-$, the evaporation rate is already relatively high, requiring a higher concentration of sulfuric acid to allow a collision before the cluster evaporates. The charged pure sulfuric acid pentamer, $(H_2SO_4)_4 \cdot HSO_4^-$, is not stable, with an evaporation rate of $1.85 \times 10^3\ s^{-1}$. Therefore, as in the neutral case (Ortega et al., 2012), additional stabilizing compounds are needed to allow further additions of sulfuric acid molecule to the cluster.

Ammonia evaporation rates from $HSO_4^- \cdot NH_3$ and $H_2SO_4 \cdot HSO_4^- \cdot NH_3$ clusters are around 10^{10}–$10^{11}\ s^{-1}$. For the $(H_2SO_4)_2 \cdot HSO_4^- \cdot NH_3$ cluster, the ammonia evaporation rate is close to $10^5\ s^{-1}$, and thus the ammonia concentration needs to be of the order of $10^{14}\ cm^{-3}$ (around 4 ppm) for collisions to be frequent enough to retain ammonia in the cluster after charging. The $(H_2SO_4)_3 \cdot HSO_4^- \cdot NH_3$ cluster is equally stable as the pure charged four sulfuric acid cluster $(H_2SO_4)_3 \cdot HSO_4^-$ and the $(H_2SO_4)_3 \cdot HSO_4^- \cdot (NH_3)_2$ is the most stable negatively charged cluster with four sulfuric acid molecules. Both the $(H_2SO_4)_4 \cdot HSO_4^- \cdot NH_3$ and $(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_2$ clusters more stable than the pure five sulfuric acid cluster, $(H_2SO_4)_4 \cdot HSO_4^-$. In case of the $(H_2SO_4)_4 \cdot HSO_4^- \cdot NH_3$ cluster, H_2SO_4 will evaporate faster than ammonia from the cluster. The stability of the $HSO_4^- \cdot (CH_3)_2NH$ cluster is similar to the corresponding ammonia cluster. However, in DMA-containing clusters, stability increases much faster as the number of sulfuric acid molecules increases than in ammonia-containing clusters. In the case of DMA clusters, already the $(H_2SO_4)_2 \cdot HSO_4^- \cdot (CH_3)_2NH$ cluster is close in stability to the pure charged three sulfuric acid cluster, and $(H_2SO_4)_3 \cdot HSO_4^- \cdot ((CH_3)_2NH)_2$ is more stable than $(H_2SO_4)_3 \cdot HSO_4^-$cluster.

These results confirm that while sulfuric acid is able to form up to anionic trimers on its own, in a similar way to neutral clusters, some additional stabilizing compound is needed to enable further growth by addition of sulfuric acid molecules. This is not surprising, since the bisulfate ion itself is a Lewis base, and thus able to stabilize the cluster. Figure 3 compares the evaporation rates of pure neutral sulfuric acid clusters and clusters containing one stabilizing base (including the bisulfate ion as a base). In all cases one base molecule is able to stabilize only clusters with up to three sulfuric acid molecules, and additional base molecules are needed to stabilize larger clusters. HSO_4^- is able to form very stable clusters with one sulfuric acid molecule compared to DMA and NH_3, but clusters with two sulfuric acid molecules are already better stabilized by DMA. As sulfuric acid molecules are added to the cluster, the evaporation rate approaches that of pure neutral sulfuric acid clusters. Clusters containing four sulfuric acid molecules are not stabilized sufficiently by just one base, and thus the evaporation rate of clusters containing four sulfuric acids and a base is similar to the evaporation rate of the pure sulfuric acid tetramer. As already shown by Ortega et al. (2012), further base molecules are needed to stabilize larger clusters. It is not possible to add a second bisulfate ion to a small cluster due to electrostatic repulsion, but a neutral nitrogen-containing base (ammonia or DMA) can be added.

4.2 Positive clusters

In the case of positively charged clusters, according to the formation free energies calculated, the only cluster for which cluster fission processes are important is $(H_2SO_4)_4((CH_3)_2NH)_4((CH_3)_2NH_2^+)$ for which the highest evaporation rate corresponds to $(H_2SO_4)_4((CH_3)_2NH)_4((CH_3)_2NH_2^+) \rightarrow (H_2SO_4)_3((CH_3)_2NH)_3((CH_3)_2NH_2^+) + (H_2SO_4)((CH_3)_2NH)$ fission.

For each number of sulfuric acid molecules, the most stable positively charged clusters (Fig. 4) have evaporation rates below $1\,s^{-1}$. In the case of positive sulfuric acid-ammonia clusters, the most stable cluster is $(H_2SO_4)_2 \cdot (NH_3)_2 \cdot NH_4^+$. As cluster size increases, the evaporation rate increases. As in negatively charged clusters, DMA clusters are more stable than ammonia clusters. For DMA the most stable cluster is $H_2SO_4 \cdot (CH_3)_2NH \cdot (CH_3)_2NH_2^+$, and, as in the case of ammonia, as cluster size increases the evaporation rate increases. The acid : base stoichiometry of positively charged clusters is the same for ammonia and DMA. The most stable clusters are formed by the cation and an equal number of sulfuric acid and base molecules. In this case NH_4^+ and $(CH_3)_2NH_2^+$ cations (or technically the protons bound to the nitrogen atoms) are Lewis acids, so there will be a competition for bases between the cation and the sulfuric acid, instead of a competition between bases for the available acids.

4.3 Charging neutral clusters

To evaluate the effect of charging in the detection of neutral clusters by mass spectrometry techniques, we have compared the evaporation rates of the most stable base-containing neutral clusters to the evaporation rates of the charged clusters obtained by adding or removing a proton from the neutral clusters (Figs. 5–7).

Figure 5 shows the most stable ammonia–containing neutral clusters and the corresponding negatively charged ones. We can see that if the most stable neutral ammonia-containing clusters get charged, their charged counterpart is unstable. For example, the $(H_2SO_4)_2 \cdot NH_3$ cluster is stable, but its negatively charged counterpart, $H_2SO_4 \cdot HSO_4^- \cdot NH_3$, is extremely unstable and an ammonia molecule will evaporate, resulting in the charged pure sulfuric acid dimer. The situation for charged clusters containing three sulfuric acid molecules is similar. Neutral ammonia-containing clusters will lose the ammonia molecules when charged, and will be detected as pure charged trimers. Once the cluster has four sulfuric acid molecules, only one ammonia molecule will evaporate from the cluster. Thus, although some ammonia molecules will stay in the cluster, the composition of the resulting charged cluster will be different from the original neutral cluster.

In the case of DMA-containing clusters the most stable neutral cluster, $(H_2SO_4)_2 \cdot (CH_3)_2NH$, will lose the DMA molecule when it is charged, ending up as a charged pure sulfuric acid cluster. The main difference between ammonia and DMA clusters is that three sulfuric acid molecules are enough to keep some DMA molecules in the cluster after negative charging. As in the case of ammonia, the number of DMA molecules in the neutral cluster will change when charged. This has important implications, since, according to recent modeling studies (Olenius et al., 2013b; Kupiainen-Määttä et al., 2013), $H_2SO_4 \cdot DMA$ and $(H_2SO_4)_2 \cdot DMA$ clusters might be relatively abundant under atmospheric conditions, but they will not be detected by mass spectrometry techniques as DMA-containing clusters.

Charging base-containing clusters positively will also affect their composition in most cases (Fig. 6). The $H_2SO_4 \cdot NH_4^+$ cluster is stable, so $H_2SO_4 \cdot NH_3$ will not evaporate back into monomers after becoming positively charged. Larger neutral clusters will not remain stable when charged positively. $(H_2SO_4)_2 \cdot NH_4^+$ cluster will evaporate one sulfuric acid molecule, leading to the stable $H_2SO_4 \cdot NH_4^+$ cluster. In the case of neutral clusters, the number of sulfuric acid molecules in stable clusters is one higher than the number of ammonia molecules, while in the most stable positively charged clusters the number of ammonia molecules (including the NH_4^+ ion) is one higher than number of sulfuric acid molecules. Therefore clusters containing three and four sulfuric acids need to evaporate two sulfuric acid molecules after being charged to reach a favorable composition.

In the case of DMA-containing clusters, all the charged counterparts of the most stable neutral clusters are unstable. $H_2SO_4 \cdot (CH_3)_2NH_2^+$ and $(H_2SO_4)_2 \cdot (CH_3)_2NH_2^+$ clusters will most probably evaporate into monomers. In the case of larger clusters, which in the neutral case favour the same number of DMA and sulfuric acid molecules, positively charged clusters will evaporate one sulfuric acid molecule, leading to the formation of the stable clusters $(H_2SO_4)_2 \cdot (CH_3)_2NH \cdot (CH_3)_2NH_2^+$ and $(H_2SO_4)_2 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$.

Figure 7 represents schematically the effect of charging most stable neutral ammonia/DMA-containing clusters. We have included in the figure evaporation paths until the resulting cluster has an evaporation rate smaller than $10\,s^{-1}$. This limit is arbitrary and has been chosen just to make the scheme simpler. The relative concentration of different clusters is not only determined by their evaporation rates but also by the collision frequency of different species with the cluster. On other words, not always the most stable cluster (in terms of evaporation rate) will be the most abundant. Although in the case of clusters with extremely high evaporation rates, for example in the case of $HSO_4^- \cdot NH_3$, the concentration of those clusters will be close to zero in atmospherically relevant conditions. In a similar way, if the evaporation rate is close to zero, like for $H_2SO_4 \cdot HSO_4^-$ cluster, the cluster will not evaporate under atmospherically relevant conditions.

5 Conclusions

In this work we present the evaporation rates of both positively and negatively charged sulfuric acid – ammonia and sulfuric acid – DMA clusters. We found that the most stable positively charged base-containing clusters have evaporation rates below $1\,s^{-1}$, while in the case of the smallest negatively charged clusters the pure sulfuric acid clusters are more stable than any base-containing clusters, and bases become important only at larger cluster sizes. DMA-containing positively charged clusters are more stable than the ammonia-containing clusters, and in both cases the stability decreases when the cluster size increases. In the case of negatively charged clusters, HSO_4^- acts as a Lewis base, and is able to stabilize the smallest cluster effectively. Similarly as for neutral clusters, one base is able to bind to only a few (around two) sulfuric acid molecules. To prevent the fast evaporation of subsequently added sulfuric acid molecules, the addition of further base molecules is needed. In the case of HSO_4^-, the addition of a second ion is not possible due to electrostatic repulsion, and thus an electrically neutral base molecule is needed. This base competition makes base-containing negatively charged clusters unstable until they reach certain a number of sulfuric acid molecules. Ammonia-containing clusters need four sulfuric acid molecules (including the bisulfate ion) to prevent the evaporation of the ammonia molecule from the cluster, while only three acids are needed in the case of DMA-containing clusters.

We have studied how charging processes (in this case, addition or removal of one proton e.g. by chemical ionization) affect cluster composition by comparing the evaporation rates of the most stable neutral sulfuric acid–ammonia and sulfuric acid–DMA clusters to the evaporation rates of the corresponding charged clusters. Our calculations show that only the $(H_2SO_4) \cdot NH_3$ cluster will retain the same acid : base ratio after charging, becoming $(H_2SO_4) \cdot NH_4^+$. The composition of the rest of the base-containing clusters will change after they are positively charged. All positively charged clusters will retain their base molecules, but will lose some number of sulfuric acid molecules. After becoming negatively charged, neutral ammonia-containing clusters with one to three sulfuric acid molecules will lose all ammonia molecules. In the case of DMA-containing clusters, one and two sulfuric acid clusters will lose all DMA molecules after charging. These results are in good agreement with experiments by Kirkby et al. (2011) and Almeida et al. (2013) in which the smallest detected ammonia containing- and DMA-containing negatively charged clusters contained four and three sulfuric acid molecules, respectively.

In view of these results, experimental Chemical Ionization-APi-TOF-MS measurements of both positive and negative clusters distributions combined with cluster kinetic models like ACDC (McGrath et al., 2012; Olenius et al., 2013a) can be used to link the observed charged cluster distribution with the corresponding neutral cluster distribution.

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References

Ahlrichs, R., Bar, M., Häser, J., Horn, H., and Kölmel C.: Electronic structure calculations on workstation computers: the program system TURBOMOLE, Chem. Phys. Lett., 162, 165–169, 1989.

Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, Ale., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., McGrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F.,Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H., and Kirkby, J.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, Nature, 502, 359–363, 2013.

Becke, A. D.: Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys., 98, 5648–5652, 1993.

Benson, D. R., Yu, J. H., Markovich, A., and Lee, S.-H.: Ternary homogeneous nucleation of H_2SO_4, NH_3, and H_2O under conditions relevant to the lower troposphere, Atmos. Chem. Phys., 11, 4755–4766, doi:10.5194/acp-11-4755-2011, 2011.

Chapman, S. and Cowling, T. G.: The Mathematical Theory of Non Uniform Gases, University Press, Cambridge, 1970.

Dunning Jr., T. H., Peterson, K. A., and Wilson, A. K.: Gaussian basis sets for use in correlated molecular calculations. X. The atoms aluminum through argon revisited, J. Chem. Phys., 114, 9244–9253, 2001.

Ehn, M., Junninen, H., Petäjä, T., Kurtén, T., Kerminen, V.-M., Schobesberger, S., Manninen, H. E., Ortega, I. K., Vehkamäki, H., Kulmala, M., and Worsnop, D. R.: Composition and temporal behavior of ambient ions in the boreal forest, Atmos. Chem. Phys., 10, 8513–8530, doi:10.5194/acp-10-8513-2010, 2010.

Friedlander, S. K.: Smoke, Dust and Haze, John Wiley & Sons, New York, 1977.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery Jr., J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J.,Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J., and Fox, D. J.: Gaussian 09, Revision B01, Gaussian, Inc., Wallingford CT, 2009.

Froyd, K. D. and Lovejoy, E. R.: Experimental thermodynamics of cluster ions composed of H_2SO_4 and H_2O. 2. Measurements and ab initio structures of negative ions, J. Phys. Chem. A, 107, 9812–9824, 2003.

Hattig, C. and Weigend, F.: CC2 excitation energy calculations on large molecules using the resolution of the identity approximation, J. Chem. Phys., 113, 5154–5161, 2000.

IPCC, The Intergovernmental Panel on Climate Change: Climate Change 2007: The Physical Science Basis, Cambridge University Press, New York, 2007.

Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin III, R. L., Kulmala, M., and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF, Atmos. Chem. Phys., 12, 4117–4125, doi:10.5194/acp-12-4117-2012, 2012.

Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition, Atmos. Meas. Tech., 3, 1039–1053, doi:10.5194/amt-3-1039-2010, 2010.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagne, S., Ickes, L., Kurten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkila, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petaja, T., Schnitzhofer, R., Seinfeld, J. H., Sipila, M., Stozhkov, Y., Stratmann, F., Tome, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429, doi:10.1038/nature10343, 2011.

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Jarvinen, E., Aijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkila, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin, R. L., Duplissy, J., Vehkamaki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurten, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V. M., and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation, Science, 339, 943–946, doi:10.1126/science.1227385, 2013.

Kupiainen, O., Ortega, I. K., Kurtén, T., and Vehkamäki, H.: Amine substitution into sulfuric acid – ammonia clusters, Atmos. Chem. Phys., 12, 3591–3599, doi:10.5194/acp-12-3591-2012, 2012.

Kupiainen-Määttä, O., Olenius, T., Kurtén, T., and Vehkamäki, H.: CIMS sulfuric acid detection efficiency enhanced by amines due to higher dipole moments: a computational study. J. Phys. Chem. A, 117, 14109–14119, 2013.

Kurtén, T.: A comment on Nadytko et al.: Amines in the Earth's atmosphere: a density functional theory study of the thermochemistry of pre-nucleation cluster, Entropy, 2011, 13, 554–569, Entropy, 13, 912–923, 2011.

Kurtén, T., Noppel, M., Vehkamäki, H., Salonen, M., and Kulmala, M.: Quantum chemical studies of hydrate formation of H_2SO_4 and HSO_4^-, Boreal Environ. Res., 12, 431–453, 2007.

Kurtén, T., Loukonen, V., Vehkamäki, H., and Kulmala, M.: Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia, Atmos. Chem. Phys., 8, 4095–4103, doi:10.5194/acp-8-4095-2008, 2008.

Kurtén, T., Petäjä, T., Smith, J., Ortega, I. K., Sipilä, M., Junninen, H., Ehn, M., Vehkamäki, H., Mauldin, L., Worsnop, D. R., and Kulmala, M.: The effect of H_2SO_4 – amine clustering on chemical ionization mass spectrometry (CIMS) measurements of gas-phase sulfuric acid, Atmos. Chem. Phys., 11, 3007–3019, doi:10.5194/acp-11-3007-2011, 2011.

Loukonen, V., Kurtén, T., Ortega, I. K., Vehkamäki, H., Pádua, A. A. H., Sellegri, K., and Kulmala, M.: Enhancing effect of dimethylamine in sulfuric acid nucleation in the presence of water – a computational study, Atmos. Chem. Phys., 10, 4961–4974, doi:10.5194/acp-10-4961-2010, 2010.

Mäkelä, J. M., Yli-Koivisto, S., Hiltunen, V., Seidl, W., Swietlicki, E., Teinila, K., Sillanpää, M., Koponen, I. K., Paatero, J., Rosman, K., and Hameri, K.: Chemical composition of aerosol during particle formation events in boreal forest, Tellus B, 53, 380–393, doi:10.1034/j.1600-0889.2001.530405.x, 2001

McGrath, M. J., Olenius, T., Ortega, I. K., Loukonen, V., Paasonen, P., Kurtén, T., Kulmala, M., and Vehkamäki, H.: Atmospheric Cluster Dynamics Code: a flexible method for solution of the birth-death equations, Atmos. Chem. Phys., 12, 2345–2355, doi:10.5194/acp-12-2345-2012, 2012.

Merikanto, J., Napari, I., Vehkamäki, H., Anttila, T., and Kulmala, M.: New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions, J. Geophys. Res., 112, D15207, doi:10.1029/2006JD007977, 2007.

Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S.: Impact of nucleation on global CCN, Atmos. Chem. Phys., 9, 8601–8616, doi:10.5194/acp-9-8601-2009, 2009.

Montgomery, J. A., Frisch, M. J., Ochterski, J. W., and Petersson, G. A.: A complete basis set model chemistry. VI. Use of density functional geometries and frequencies, J. Chem. Phys., 110, 2822–2827, 1999.

Nadykto, A. B., Yu, F. Q., Jakovleva, M. V., Herb, J., and Xu, Y. S.: Amines in the Earth's atmosphere: a density functional theory study of the thermochemistry of pre-nucleation clusters, Entropy, 13, 554–569, 2011.

Olenius, T., Schobesberger, S., Kupiainen-Määtä, O., Franchin, A., Junninen, H., Ortega, I. K., Kurtén T., Loukonen, V., Worsnop, D. R., Kulmala, M., and Vehkamäki, H.: Comparing simulated and experimental molecular cluster distributions, Faraday Discuss., 165, 75–89, doi:10.1039/C3FD00031A, 2013a.

Olenius, T., Kupiainen, O., Ortega, I. K., Kurtén, T., and Vehkamäki, H.: Free energy barrier in the growth of sulfuric acid-ammonia and sulfuric acid-dimethylamine clusters, J. Chem. Phys., 139, 084312, doi:10.1063/1.4819024, 2013b.

Ortega, I. K., Kurtén, T., Vehkamäki, H., and Kulmala, M.: The role of ammonia in sulfuric acid ion induced nucleation, Atmos. Chem. Phys., 8, 2859–2867, doi:10.5194/acp-8-2859-2008, 2008.

Ortega, I. K., Kupiainen, O., Kurtén, T., Olenius, T., Wilkman, O., McGrath, M. J., Loukonen, V., and Vehkamäki, H.: From quantum chemical formation free energies to evaporation rates, Atmos. Chem. Phys., 12, 225–235, doi:10.5194/acp-12-225-2012, 2012.

Ruusuvuori, K., Hietala, P., Kupiainen-Määttä, O., Kurtén, T., and Vehkamäki, V.: The charging of amine containing clusters using protonated acetone, Atmos. Meas. Tech. Discuss., submitted, 2013.

Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin, R. L. I., Hyvarinen, A.-P., Lihavainen, H., and Kulmala, M.: The role of sulfuric acid in atmospheric nucleation, Science, 327, 1243–1246, 2010.

Smith, J. N., Barsanti, K. C., Friedli, H. R., Ehn, M., Kulmala, M., Collins, D. R., Scheckman, J. H., Williams, B. J., and McMurry, P. H.: Observations of ammonium salts in atmospheric nanoparticles and possible climatic implications, P. Natl. Acad. Sci. USA, 107, 6634–6639, 2010.

Su, T. and Bowers, M. T.: Theory of ion-polar molecule collisions. Comparison with experimental charge transfer reactions of rare gas ions to geometric isomers of difluorobenzene and dichloroethylene, J. Chem. Phys., 58, 3027, doi:10.1063/1.1679615, 1973.

Weber, R. J., Marti, J. J., McMurry, P. H., Eisele, F. L., Tanner, D. J., and Jefferson, A.: Measured atmospheric new particle formation rates: Implications for nucleation mechanisms, Chem. Eng. Commun., 151, 53–64, doi:10.1080/00986449608936541, 1996.

Zhao, J., Smith, J. N., Eisele, F. L., Chen, M., Kuang, C., and McMurry, P. H.: Observation of neutral sulfuric acid-amine containing clusters in laboratory and ambient measurements, Atmos. Chem. Phys., 11, 10823–10836, doi:10.5194/acp-11-10823-2011, 2011.

Table 1. Evaporation rate of H_2SO_4 from negatively charged sulfuric acid clusters at 298.15 K calculated using B3RICC2 and experimental formation free energies from Lovejoy et al. (2003).

Cluster	Theoretical evaporation rate (s^{-1})	Experimental evaporation rate (s^{-1})
$(H_2SO_4)\cdot HSO_4^-$	1.77×10^{-15}	1.60×10^{-11}
$(H_2SO_4)_2\cdot HSO_4^-$	3.67×10^{-3}	8.16×10^{-3}
$(H_2SO_4)_3\cdot HSO_4^-$	1.58×10^{1}	5.29
$(H_2SO_4)_4\cdot HSO_4^-$	1.85×10^{3}	2.5×10^{2}

Table 2a. Schematic diagram of the negatively charged clusters included in this study. NH_3 indicates ammonia-containing and DMA indicates DMA-containing clusters.

	1 base	2 bases	3 bases	4 bases
HSO_4^-	NH_3 DMA			
$(H_2SO_4) \cdot HSO_4^-$	NH_3 DMA	DMA		
$(H_2SO_4)_2 \cdot HSO_4^-$	NH_3 DMA	NH_3 DMA	DMA	
$(H_2SO_4)_3 \cdot HSO_4^-$	NH_3 DMA	NH_3 DMA	NH_3 DMA	DMA
$(H_2SO_4)_4 \cdot HSO_4^-$	NH_3	NH_3	NH_3	NH_3

Table 2b. Schematic diagram of the positively charged clusters included in this study. NH_3 indicates ammonia-containing and DMA indicates DMA-containing clusters.

	H^+ + 1 base	H^+ + 2 bases	H^+ + 3 bases	H^+ + 4 bases	H^+ + 5 bases
0 acids	NH_3 DMA	NH_3 DMA	NH_3 DMA		
H_2SO_4	NH_3 DMA	NH_3 DMA	NH_3 DMA		
$(H_2SO_4)_2$	NH_3 DMA	NH_3 DMA	NH_3 DMA	NH_3 DMA	
$(H_2SO_4)_3$			NH_3 DMA	NH_3 DMA	
$(H_2SO_4)_4$			NH_3 DMA	NH_3 DMA	NH_3 DMA

Table 3. Highest evaporation rate and evaporating molecule/cluster at 298.15 K for different negatively charged clusters studied.

Cluster	Evaporation rate (s^{-1})	Evaporating molecule/cluster
$H_2SO_4 \cdot HSO_4^-$	1.77×10^{-15}	H_2SO_4
$(H_2SO_4)_2 \cdot HSO_4^-$	3.67×10^{-3}	H_2SO_4
$(H_2SO_4)_3 \cdot HSO_4^-$	1.58×10^{1}	H_2SO_4
$(H_2SO_4)_4 \cdot HSO_4^-$	1.85×10^{3}	H_2SO_4
$HSO_4^- \cdot NH_3$	3.09×10^{11}	NH_3
$H_2SO_4 \cdot HSO_4^- \cdot NH_3$	1.46×10^{10}	NH_3
$(H_2SO_4)_2 \cdot HSO_4^- \cdot NH_3$	1.15×10^{5}	NH_3
$(H_2SO_4)_3 \cdot HSO_4^- \cdot NH_3$	2.00×10^{1}	NH_3
$(H_2SO_4)_4 \cdot HSO_4^- \cdot NH_3$	1.25	H_2SO_4
$(H_2SO_4)_2 \cdot HSO_4^- \cdot (NH_3)_2$	8.51×10^{4}	NH_3
$(H_2SO_4)_3 \cdot HSO_4^- \cdot (NH_3)_2$	7.95	NH_3
$(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_2$	2.51×10^{-1}	NH_3
$(H_2SO_4)_3 \cdot HSO_4^- \cdot (NH_3)_3$	1.60×10^{3}	NH_3
$(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_3$	6.88×10^{-3}	NH_3
$(H_2SO_4)_4 \cdot HSO_4^- \cdot (NH_3)_4$	2.30×10^{9}	NH_3
$HSO_4^- \cdot (CH_3)_2NH$	7.66×10^{9}	$(CH_3)_2NH$
$H_2SO_4 \cdot HSO_4^- \cdot (CH_3)_2NH$	4.90×10^{2}	$(CH_3)_2NH$
$(H_2SO_4)_2 \cdot HSO_4^- \cdot (CH_3)_2NH$	4.95×10^{-2}	$(CH_3)_2NH$
$(H_2SO_4)_3 \cdot HSO_4^- \cdot (CH_3)_2NH$	1.03	$(H_2SO_4)_2 \cdot (CH_3)_2NH$
$H_2SO_4 \cdot HSO_4^- \cdot ((CH_3)_2NH)_2$	3.58×10^{8}	$(CH_3)_2NH$
$(H_2SO_4)_2 \cdot HSO_4^- \cdot ((CH_3)_2NH)_2$	2.49×10^{-1}	$(CH_3)_2NH$
$(H_2SO_4)_3 \cdot HSO_4^- \cdot ((CH_3)_2NH)_2$	9.25×10^{-4}	$(H_2SO_4)_2 \cdot ((CH_3)_2NH)_2$
$(H_2SO_4)_2 \cdot HSO_4^- \cdot ((CH_3)_2NH)_3$	2.30×10^{4}	$(CH_3)_2NH$
$(H_2SO_4)_3 \cdot HSO_4^- \cdot ((CH_3)_2NH)_3$	2.91×10^{1}	$(CH_3)_2NH$
$(H_2SO_4)_3 \cdot HSO_4^- \cdot ((CH_3)_2NH)_4$	7.22×10^{1}	$(CH_3)_2NH$

Table 4. Highest evaporation rate and evaporating molecule/cluster at 298.15 K for different positively charged clusters studied.

Cluster	Evaporation rate (s^{-1})	Evaporating molecule/cluster
$H_2SO_4 \cdot NH_4^+$	2.31×10^{-1}	H_2SO_4
$(H_2SO_4)_2 \cdot NH_4^+$	1.83×10^{2}	H_2SO_4
$NH_3 \cdot NH_4^+$	3.98×10^{-5}	NH_3
$H_2SO_4 \cdot NH_3 \cdot NH_4^+$	1.81×10^{-2}	H_2SO_4
$(H_2SO_4)_2 \cdot NH_3 \cdot NH_4^+$	8.03×10^{-1}	H_2SO_4
$(H_2SO_4)_3 \cdot NH_3 \cdot NH_4^+$	2.72×10^{2}	H_2SO_4
$(NH_3)_2 \cdot NH_4^+$	1.56×10^{4}	NH_3
$H_2SO_4 \cdot (NH_3)_2 \cdot NH_4^+$	7.19×10^{2}	NH_3
$(H_2SO_4)_2 \cdot (NH_3)_2 \cdot NH_4^+$	1.69×10^{-5}	NH_3
$(H_2SO_4)_3 \cdot (NH_3)_2 \cdot NH_4^+$	1.48×10^{2}	H_2SO_4
$(H_2SO_4)_4 \cdot (NH_3)_2 \cdot NH_4^+$	3.70×10^{3}	H_2SO_4
$(H_2SO_4)_2 \cdot (NH_3)_3 \cdot NH_4^+$	1.24×10^{4}	NH_3
$(H_2SO_4)_3 \cdot (NH_3)_3 \cdot NH_4^+$	4.21×10^{-4}	NH_3
$(H_2SO_4)_4 \cdot (NH_3)_3 \cdot NH_4^+$	7.72×10^{1}	H_2SO_4
$(H_2SO_4)_3 \cdot (NH_3)_4 \cdot NH_4^+$	1.66×10^{4}	NH_3
$(H_2SO_4)_4 \cdot (NH_3)_4 \cdot NH_4^+$	5.01×10^{-1}	NH_3
$(H_2SO_4)_5 \cdot (NH_3)_4 \cdot NH_4^+$	7.85×10^{-1}	H_2SO_4
$(H_2SO_4) \cdot (CH_3)_2NH_2^+$	5.01×10^{2}	H_2SO_4
$(H_2SO_4)_2 \cdot (CH_3)_2NH_2^+$	4.64×10^{1}	H_2SO_4
$(CH_3)_2NH \cdot (CH_3)_2NH_2^+$	1.56×10^{-2}	$(CH_3)_2NH$
$H_2SO_4 \cdot (CH_3)_2NH \cdot (CH_3)_2NH_2^+$	1.80×10^{-10}	H_2SO_4
$(H_2SO_4)_2 \cdot (CH_3)_2NH \cdot (CH_3)_2NH_2^+$	1.07	H_2SO_4
$((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	9.78×10^{3}	$(CH_3)_2NH$
$H_2SO_4 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	2.54×10^{-2}	$(CH_3)_2NH$
$(H_2SO_4)_2 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	3.80×10^{-10}	H_2SO_4
$(H_2SO_4)_3 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	8.23×10^{1}	H_2SO_4
$(H_2SO_4)_4 \cdot ((CH_3)_2NH)_2 \cdot (CH_3)_2NH_2^+$	1.14×10^{-1}	H_2SO_4
$(H_2SO_4)_2 \cdot ((CH_3)_2NH)_3 \cdot (CH_3)_2NH_2^+$	1.45×10^{-2}	$(CH_3)_2NH$
$(H_2SO_4)_3 \cdot ((CH_3)_2NH)_3 \cdot (CH_3)_2NH_2^+$	9.60×10^{-9}	H_2SO_4
$(H_2SO_4)_4 \cdot ((CH_3)_2NH)_3 \cdot (CH_3)_2NH_2^+$	2.79×10^{3}	H_2SO_4
$(H_2SO_4)_4 \cdot ((CH_3)_2NH)_4 \cdot (CH_3)_2NH_2^+$	7.66×10^{-6}	$H_2SO_4 \cdot (CH_3)_2NH$

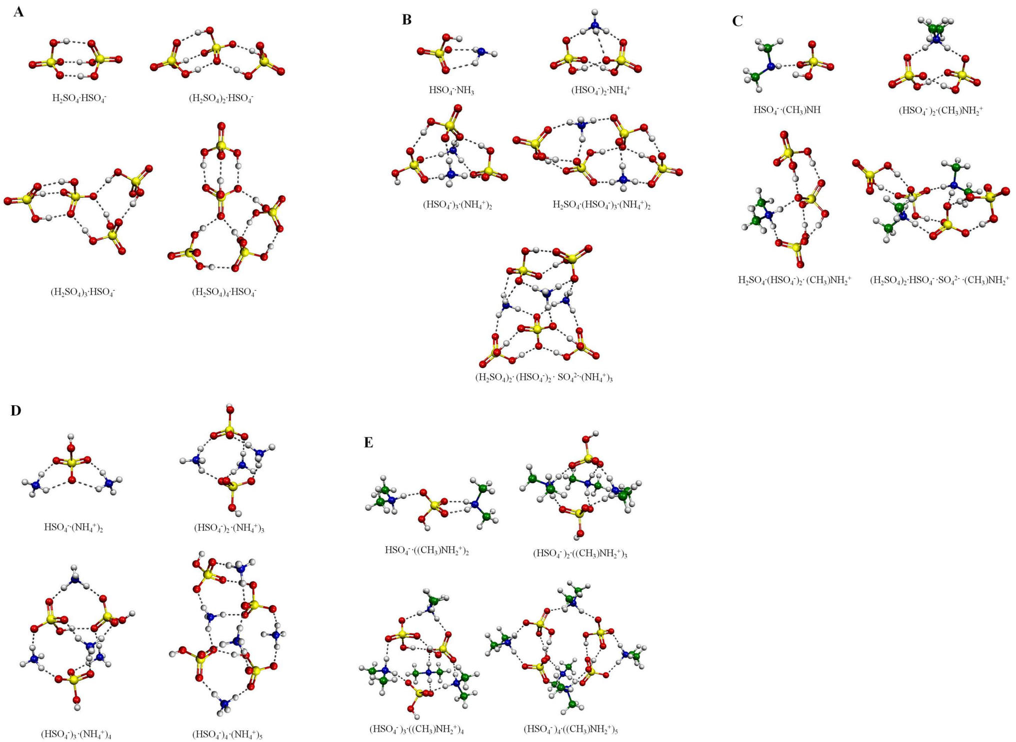

Fig. 1. Structures of clusters with one to four/five sulfuric acid molecules and the most favorable number of base molecules (those with the lowest evaporation rate) for: **(A)** negatively charged sulfuric acid clusters, **(B)** negatively charged ammonia-containing clusters, **(C)** negatively charged DMA-containing clusters, **(D)** positively charged ammonia-containing clusters and **(E)** positively charged DMA-containing clusters. Red spheres represent oxygen atoms, yellow spheres represent sulfur atoms, blue spheres represent nitrogen atoms, withe spheres represent hydrogen atoms and green spheres represent carbon atoms.

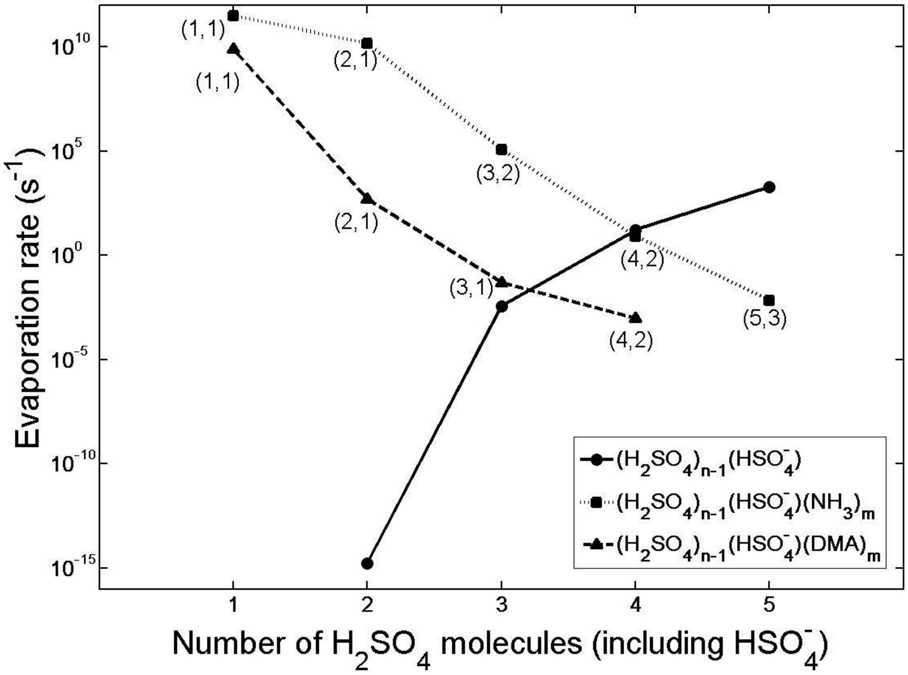

Fig. 2. Evaporation rates at 298.15 K (s^{-1}) for most stable negatively charged clusters vs. the number of sulfuric acid molecules in the cluster including the bisulfate ion, that is, 1 corresponds to HSO_4^-, 2 corresponds to H_2SO_4 HSO_4^- etc. Numbers in parentheses indicate the composition of the cluster (acids, bases). Solid line represents pure sulfuric acid clusters, dashed line represents sulfuric acid-DMA clusters and dotted line represents sulfuric acid-ammonia clusters.

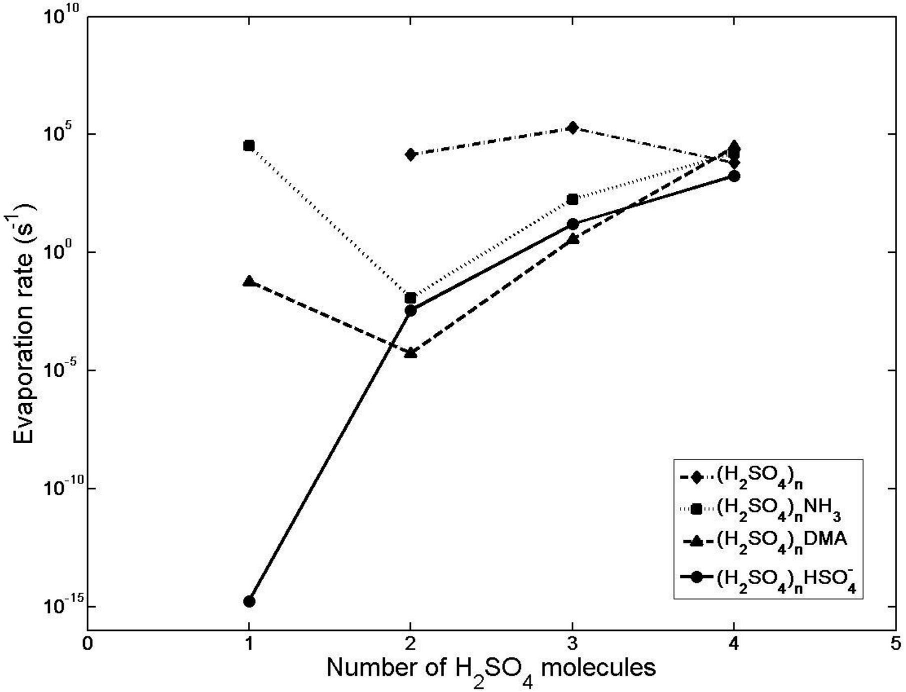

Fig. 3. Evaporation rates at 298.15 K (s^{-1}) of sulfuric acid clusters containing up to one Lewis base vs. the number of sulfuric acid molecules in the cluster (not including the bisulfate ion). Dash-dotted line represents pure neutral sulfuric acid clusters, dotted line represents neutral sulfuric acid clusters with one ammonia molecule, dashed line represents neutral sulfuric acid clusters with one DMA molecule and solid line represents pure sulfuric acid clusters with one HSO_4^- ion. Note that unlike in Fig. 2, now 1 corresponds to $H_2SO_4 \cdot X$, 2 corresponds to $(H_2SO_4)_2 \cdot X$ etc., where X = NH_3, DMA or HSO_4^-.

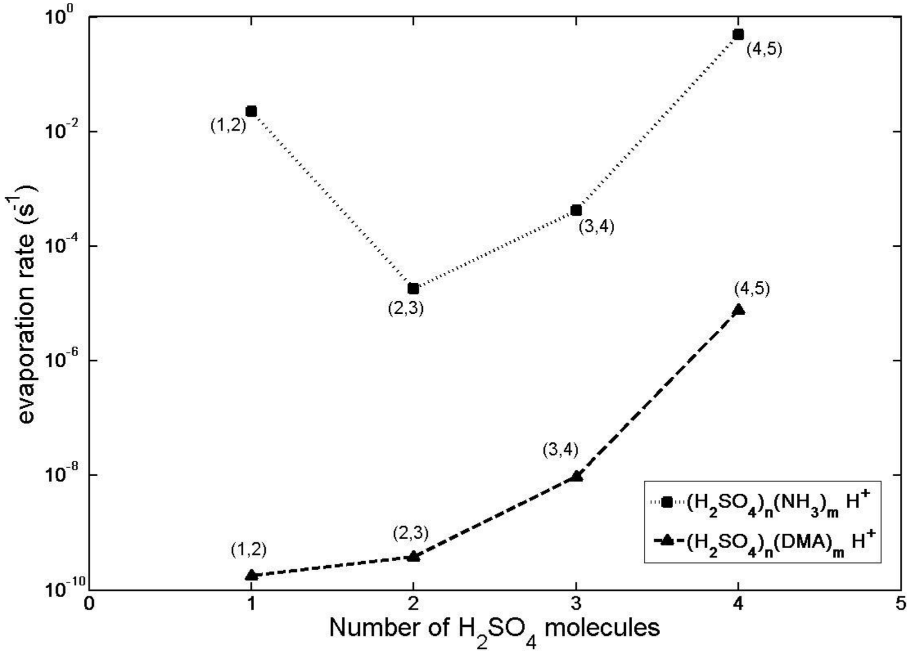

Fig. 4. Evaporation rates at 298.15 K (s^{-1}) for most stable positively charged clusters vs. the number of sulfuric acid molecules in the cluster. The numbers in parentheses indicate the composition of the cluster (acids, bases). Dashed line represents sulfuric acid-DMA clusters and dotted line represents sulfuric acid-ammonia clusters.

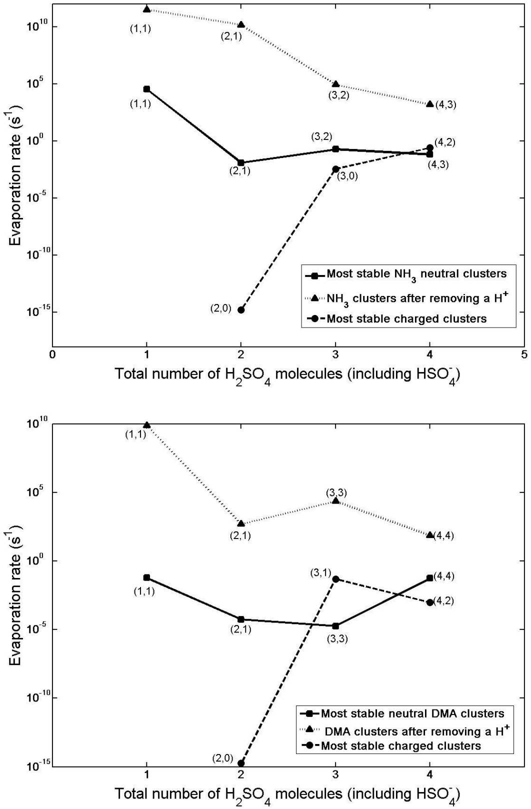

Fig. 5. Comparison of the evaporation rates at 298.15 K (s^{-1}) of neutral clusters (solid lines), negatively charged clusters obtained by removing a proton (dotted lines) and the most stable negatively charged clusters with the same number of sulfuric acid molecules (including the bisulfate ion, dashed lines). Numbers in parentheses indicates the composition of the cluster (acids, bases). Top panel: ammonia-sulfuric acid clusters. Bottom panel: DMA-sulfuric acid clusters.

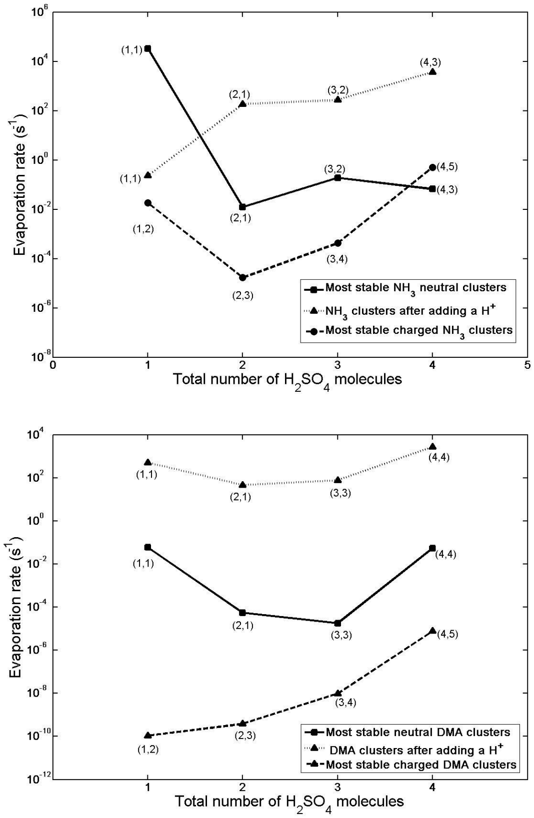

Fig. 6. Comparison of the evaporation rates at 298.15 K (s^{-1}) of neutral clusters (solid lines), positively charged clusters with one proton added (dotted lines) and the most stable positively charged clusters with the same number of sulfuric acid molecules (dashed lines). Numbers in parentheses indicates the composition of the cluster (acids, bases). Top panel: ammonia-sulfuric acid clusters. Bottom panel: DMA-sulfuric acid clusters.

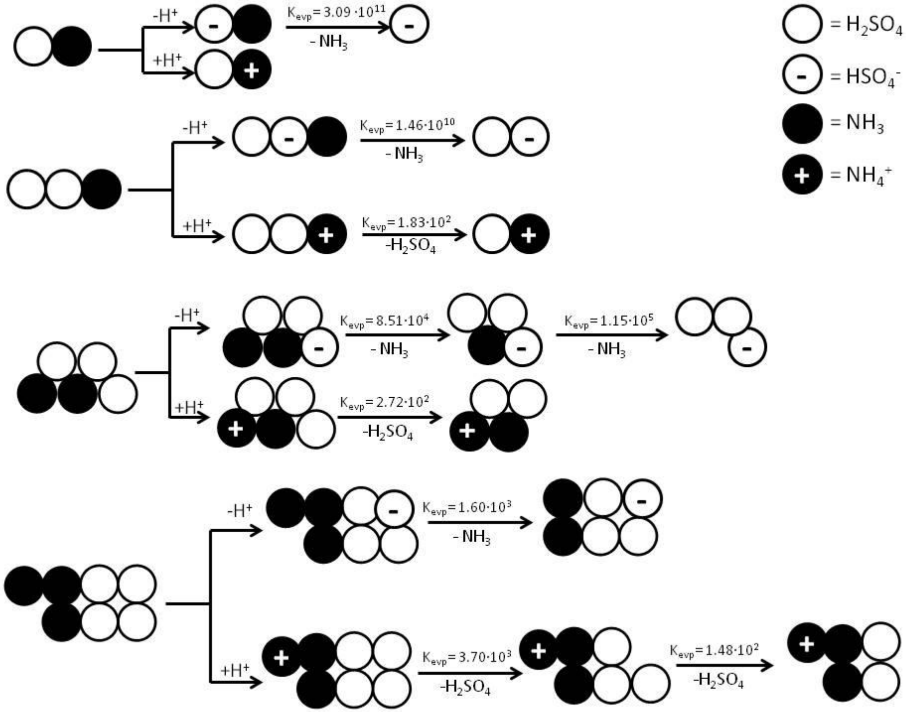

Fig. 7. Schematic representation of the evaporation pathways after charging of the most stable neutral base-containing clusters. White circles represent sulfuric acid, white circles with a minus sign represents bisulfate ion, black circles represents ammonia, black circle with a plus sing represent ammonium ion, grey circles represents dimethylamine and grey circles with a plus sign represent dimethylammonium ion.

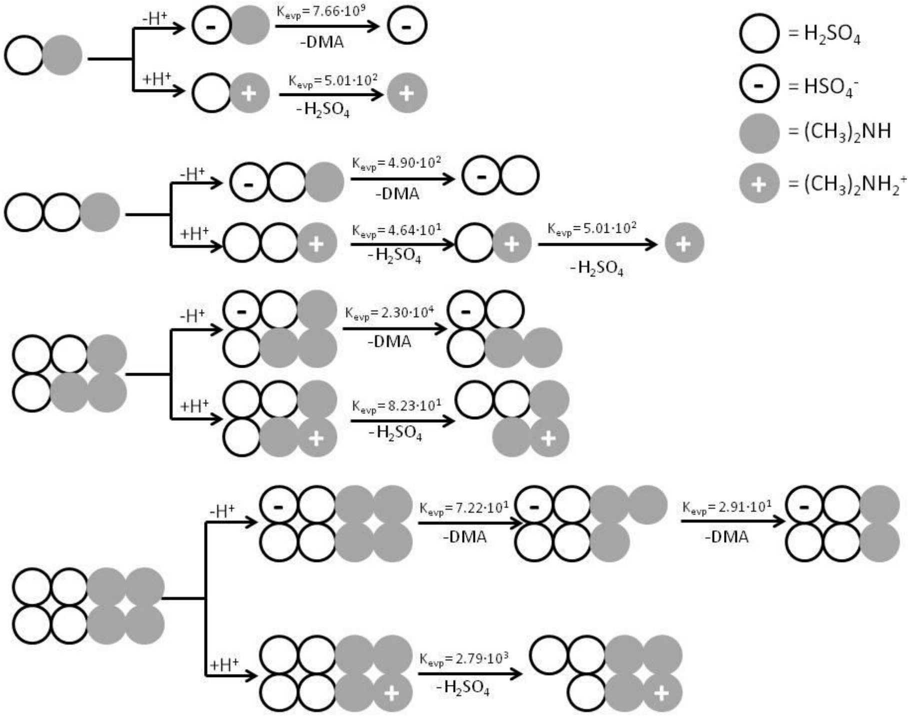

Fig. 7. Continued.